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A NEW CRITERION FOR MEASURING THE SPEED OF AERIAL PHOTOGRAPHIC EMULSIONS[1]

BY L. E. HOWLETT[2]

Abstract

Arguments are advanced to support a proposal that the speed of photographic emulsions intended for aerial photography be determined by the use of a resolving power criterion. A statistical summary of experimental results is given to show that on such a basis speed determinations can be made with sufficient reliability by different observers. The relation between speed and gamma is given for Aero Super XX.

Various Procedures for Speed Determination

Methods of assessing the speed of photographic materials have occupied a position of major importance since the beginning of photographic science. A number of procedures have been proposed. All techniques follow the general principle of defining a method for selecting an exposure that can be considered inversely proportional to the speed of the emulsion. The principle is essentially sound but the usefulness of a specific method depends on the considerations that guided its selection. These considerations should attach great importance to the specific requirements of the use to which the photographic emulsion is to be put. It is of interest to review briefly the better known criteria for selecting the significant exposure.

In the H & D system the exposure is chosen on the basis of inertia of the emulsion. For the Scheiner system the one producing the first trace of density is selected. The DIN system adopts the exposure that will produce a density of 0.1. Arguments have also been advanced for the exposure that leads to a density of 0.2 on the ground that it can be more accurately determined than the exposure giving either the first perceptible trace of density or 0.1 density.

The H & D, the DIN, and the 0.2 density systems if properly used can lead to reasonably satisfactory results for many uses of photography. Their implicit assumption that one criterion of speed assessment will be suited to all the diverse uses to which photography is applied makes them acceptable only in the absence of more logical formulations for specific purposes. The Scheiner system was originally conceived for the application of photography to astronomy. It probably has a usefulness in this field. Its employment for

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determining the speed of emulsions intended for general purpose photography is to be regretted.

More recently for general purpose photography L. A. Jones (1) worked out a fractional gradient technique for establishing the exposure on which the speed rating of an emulsion should be based. For this field of photography it is the only procedure so far advanced that takes into adequate consideration the basic user requirement. The user wants a pleasing and satisfying pictorial record of incidents or scenes. This need can be met by a print having good tone reproduction. It is therefore logical to base the speed of an emulsion on the minimum exposure required to produce a print considered excellent by a large representative group of those practising or interested in amateur photography. Having determined by this subjective method the minimum exposure needed to make an excellent print, the equivalent sensitometric speed criterion was defined. The reliability of speed ratings determined by this method for general purpose photography is now recognized and its use is continually expanding.

A Resolving Power Criterion of Speed for Aerial Photography

Large quantities of film are required and will continue to be required for aerial photography. Consequently there is an urgent need for a logical criterion of speed for this application.

It is fortunate that in most aerial photography the essential user requirement can be precisely formulated without reference to an average subjective judgment. The majority of aerial photographs are taken either for survey or military reconnaissance. Both applications either for economic or military reasons require the extraction of the maximum amount of information from the photographs. Accordingly this is the factor that must guide the selection of a speed criterion.

A limited number of aerial photographs are taken for pictorial purposes. Formulation of emulsion speeds in the latter connection would be properly based on a modification of the fractional gradient method.

The maximum amount of information obtained from a photograph depends among other important factors on the resolving power of the photographic material. The latter property is a function of the physical characteristics of the emulsion, the form and contrast of the pattern used to determine the resolving power, the mean developed density, and the processing technique. The mean density is a function of the photographic exposure and the processing technique.

The speed of an aerial film should be defined as inversely proportional to the minimum exposure giving either the maximum resolving power of the emulsion for an appropriate contrast or a specified fraction of that resolving power. To make the consumer's information complete there should be provided in addition to the speed rating, the processing technique used for the determination of the resolving-power–log-exposure curve and the contrast

and form of the test target. It is worth remarking that the gradient of the characteristic curve and the granularity of the emulsion are taken into account by such a criterion in a way that suits the use to which the negative material will be put.

The bearing of the physical characteristics of the emulsions on speed and resolving power is largely a matter of concern to the manufacturer, and the problem of developing improvements is perhaps best left to him. The user is concerned only with the performance of the emulsions offered to him.

In tests carried out to determine by a resolving power criterion the relative speeds of aerial photographic emulsions produced by different manufacturers, it would in general be reasonable to accept the manufacturer's recommendations for processing. In certain circumstances however it will be desirable for the user to vary this processing in order to assure himself that it leads to the optimum resolving-power–speed relation for his particular purpose. Consideration must also be given to obtaining an acceptable value of gamma if the information is ultimately to be obtained from prints. This aspect will be discussed later. Ultimately it may be found possible, as well as desirable, to specify a standard developing technique for comparative tests. This practice has been found quite feasible in the application of the fractional gradient method of determining speed for general photographic use.

The contrast of the test target must be decided after measuring the typical contrast for significant detail in aerial photographs. The contrast of such detail is generally low. It is therefore reasonable to assume that it is proper to choose a low contrast test target for determining the speed of aerial photographic emulsions.

Experimental Procedure for Applying the New Criterion

If it is accepted that obtaining maximum information is the factor of prime importance in establishing a basis for rating the speeds of aerial photographic emulsions, a simple procedure can be formulated for routine use. A step tablet can be prepared that is generally similar to conventional ones except for the fact that there is a resolving power target on each step. To increase the precision of the method the target should be duplicated or even triplicated on each step. The same contrast should exist between each target and the step forming its background. The target should be an array of patterns that, except for size, are identical. The sizes should follow a logarithmic progression. A target in which the pattern consists of lines and spaces of equal width and in which the length of the lines is at least nine times the spacing will probably be found the most acceptable.

In testing speeds such a tablet will be printed on the emulsion with all the usual controls employed in making sensitometric exposures. The quality of the light source should be equivalent to mean noon sunlight modified by the filter generally to be used with the emulsion in aerial photographic operations. The filter selected will probably be a Wratten No. 12 or its equivalent. The exposure time should be comparable with that to be employed in practice.

The information on resolving powers obtained from the carefully processed printings of the step tablet can be used to plot a curve relating resolving power to the logarithm of the exposure. The exposure on which the speed rating will be based can be determined from this curve.

Precision of the Proposed Criterion

It seems unlikely that any sound objections can be properly made against the theoretical correctness of the arguments advanced for the method. Nevertheless it was recognized when the proposal was first made in the early part of last year that a practical objection might exist to its satisfactory application, because of the uncertainty as to whether speeds could be determined by it with sufficient precision by the same observer at different times or by different observers.

With proper laboratory technique for exposing and processing the resolving power step tablets, it was reasonable to suppose that a sufficient degree of physical uniformity could be obtained. The necessary precautions are inherently similar to those that must be taken in all sensitometric work. The reproducibility of subjective judgments of the limit of resolving power seemed more open to question.

Making the step tablets requires a special technique but once developed it is not a difficult one to use. In this laboratory it has been found possible to produce them in a reliable and reproducible way. Density measurements necessary to establish the correctness of the contrast between the target and the background are no more difficult than those required in making ordinary sensitometric step tablets.

To assess the precision of the method a statistical survey has been made of results obtained by a representative group of observers. A surprising degree of precision has been shown. In fact the precision differs little if at all from that obtained by other methods for rating speed.

For the experiments a step tablet similar to the one already described was prepared. There were three identical line targets on each density step. The lines and spaces were equal and the length of the lines was nine times the separation. The size ratio between the steps was the sixth root of two. The log contrast was 0.2

Printings of the step tablet were made under carefully controlled conditions on 30 strips of Aero Super XX cut from the same roll. The exposure was 1/30 sec. The illumination was provided by a tungsten lamp operating at 2900° K modified by Wratten filters Nos. 51 and 12. Processing was carried out in D–19b under carefully controlled conditions until the value of gamma was 1.40. This value of gamma was selected because experience here and in England has shown it a desirable one when paper prints are to be used for interpretation.

The resolving powers were read with the aid of a binocular microscope. The magnification and the field brightness were set to values that favoured the reading of maximum resolving powers. Ten observers were used.

The general qualifications of the 10 observers were quite varied. Two or three had considerable experience in routine reading of resolving power targets. Some had a limited experience in such work. Others had none at all. It is believed that the composition of the group was such as to lead to a sound assessment of the average precision likely to be obtained from the resolving power method of speed assessment. The same general instructions on the reading procedure to be followed were given to all readers. Each had some preliminary practice until it was certain each understood the way in which the limit of resolving power was to be determined.

The speed was rated as inversely proportional to the exposure giving 90% of the maximum resolving power of the photographic material. A statistical analysis of the speeds as determined from the 30 strips by 10 observers was made. Table I presents the individual results obtained by each observer. Table II summarizes the statistical analysis.

TABLE I

SPEED DETERMINATIONS ON 30 SENSITOMETRIC STRIPS OF AERO SUPER XX BY 10 OBSERVERS

Strip No.	Observer										Av.
	UT	*VT*	*HL*	*MR*	*TT*	*MB*	*BC*	*JG*	*GB*	*JC*	
	Speed = Negative log E for 90% maximum resolving power										
1	1.65	1.76	1.74	1.73	1.73	1.73	1.75	1.71	1.65	1.70	1.72
2	1.68	1.75	1.70	1.69	1.75	1.69	1.64	1.68	1.66	1.68	1.69
3	1.73	1.67	1.71	1.66	1.60	1.68	1.57	1.74	1.67	1.68	1.67
4	1.61	1.74	1.76	1.73	1.64	1.74	1.71	1.77	1.83	1.68	1.72
5	1.60	1.68	1.64	1.66	1.61	1.66	1.69	1.76	1.61	1.64	1.66
6	1.60	1.70	1.69	1.65	1.60	1.69	1.68	1.69	1.70	1.62	1.66
7	1.60	1.73	1.76	1.74	1.67	1.75	1.68	1.81	1.67	1.64	1.71
8	1.71	1.76	1.79	1.73	1.68	1.73	1.66	1.65	1.69	1.68	1.71
9	1.66	1.73	1.74	1.76	1.69	1.72	1.66	1.74	1.71	1.62	1.70
10	1.47	1.82	1.75	1.72	1.75	1.72	1.77	1.64	1.64	1.63	1.69
11	1.58	1.73	1.69	1.69	1.71	1.75	1.64	1.82	1.74	1.70	1.71
12	1.64	1.80	1.67	1.67	1.77	1.76	1.62	1.66	1.55	1.62	1.68
13	1.62	1.66	1.64	1.68	1.59	1.68	1.67	1.67	1.63	1.59	1.64
14	1.58	1.64	1.62	1.71	1.65	1.62	1.63	1.67	1.79	1.66	1.66
15	1.65	1.70	1.74	1.73	1.67	1.73	1.66	1.75	1.75	1.70	1.71
16	1.48	1.63	1.66	1.72	1.63	1.68	1.63	1.74	1.69	1.64	1.65
17	1.54	1.63	1.67	1.68	1.68	1.69	1.67	1.71	1.62	1.64	1.65
18	1.63	1.61	1.68	1.54	1.60	1.72	1.52	1.65	1.68	1.56	1.61
19	1.62	1.67	1.67	1.64	1.66	1.70	1.64	1.75	1.67	1.66	1.67
20	1.55	1.71	1.64	1.70	1.66	1.70	1.65	1.73	1.64	1.63	1.66
21	1.60	1.60	1.59	1.67	1.69	1.67	1.55	1.73	1.70	1.56	1.64
22	1.62	1.64	1.67	1.67	1.62	1.74	1.72	1.71	1.60	1.66	1.67
23	1.61	1.70	1.72	1.60	1.66	1.65	1.59	1.67	1.75	1.53	1.65
24	1.62	1.70	1.64	1.61	1.66	1.66	1.61	1.63	1.65	1.53	1.63
25	1.59	1.65	1.70	1.56	1.60	1.64	1.61	1.52	1.68	1.64	1.62
26	1.58	1.64	1.75	1.62	1.62	1.64	1.63	1.65	1.68	1.57	1.64
27	1.67	1.75	1.75	1.68	1.62	1.70	1.74	1.80	1.75	1.66	1.71
28	1.61	1.65	1.75	1.70	1.72	1.74	1.53	1.68	1.71	1.66	1.68
29	1.72	1.72	1.71	1.70	1.65	1.73	1.71	1.77	1.74	1.67	1.71
30	1.65	1.71	1.73	1.60	1.66	1.71	1.55	1.75	1.78	1.56	1.67
Average	1.62	1.70	1.70	1.68	1.66	1.70	1.65	1.71	1.69	1.63	1.67

TABLE II

SUMMARY OF A STATISTICAL ANALYSIS OF TABLE I

σ = Standard deviation π = Probable error

Observer	*UT*	*VT*	*HL*	*MR*	*TT*	*MB*	*BC*	*JG*	*GB*	*JC*	Av.
Speed	1.62	1.70	1.70	1.68	1.66	1.70	1.65	1.71	1.69	1.63	1.67
σ	0.08	0.06	0.07	0.07	0.06	0.05	0.07	0.08	0.07	0.06	
π	0.05	0.04	0.04	0.05	0.04	0.03	0.05	0.05	0.05	0.04	0.04

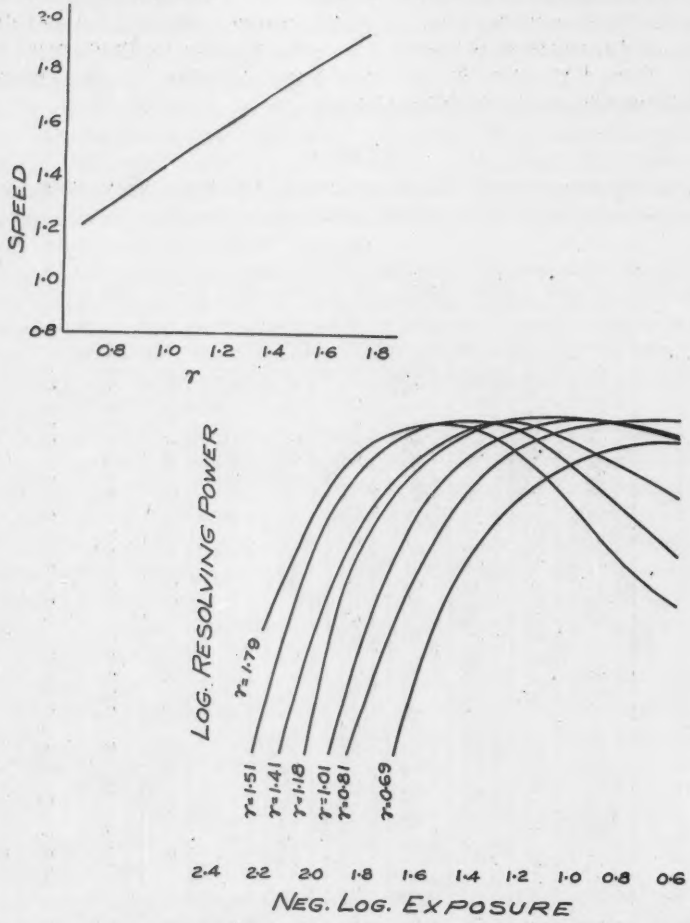

FIG. 1. *Resolving-power–exposure curves at different values of gamma for Aero Super XX, and curve showing the speed–gamma relation for the same emulsion.*

The Relation between Speed and Gamma

It was thought of interest to derive some information as to the relation between speed on the resolving power criterion and gamma. The lower part of Fig. 1 shows for Aero Super XX the log-resolving-power–log-exposure curves at seven different values of gamma. The upper graph shows the relation between speed and gamma when speed is defined as inversely proportional to the exposure yielding 90% of the maximum resolving power of the photographic material. It will be noted that speed increases continuously with gamma.

If negatives are used for securing the information from the photographs it would be logical to select a processing technique leading to the highest value of gamma, since this gives the greatest speed for the photographic material. This increase of speed would permit the use of a smaller lens aperture, with the consequent increase of over-all lens–film resolving power. If however prints are made from the negatives and used to obtain the information, a limiting value of gamma is imposed by the latitude of available papers. Under these circumstances it is necessary therefore to set a maximum acceptable value of gamma. If on account of film–paper performance, inconsistencies result from the specification of a definite value of gamma, the resolving power criterion of speed for aerial photographic emulsions might have to be applied through a film–paper combination.

Modifications of the Criterion for Special Requirements

It is of interest to note that useful modifications of the concept of emulsion speed described here can be made for special purposes. Night photography for target identification does not require great detail. The minimum acceptable resolving power and the typical contrast of test target for this application can be determined. Speeds of negative material for night photography can be taken as proportional to the maximum reciprocal exposure necessary to give the desired resolving power with the specified contrast of resolving power target. This criterion is more satisfactory than a definition that speed is proportional to the reciprocal exposure giving a certain density or a minimum gradient. The former neglects the gradient and the latter the granularity. These methods have been proposed in previous treatments of the problem. Speed for copying materials might also be defined by a suitable modification of the resolving power criterion.

Acknowledgments

The work of Mr. K. M. Baird of this laboratory in carrying out experimental work reported here and his careful preparation of the statistical analysis is gratefully acknowledged. The author also records his appreciation of the work of other colleagues in reading the resolving power step tablets.

Reference

1. JONES, L. A. J. Franklin Inst. 227 : 297-354, 497-544. 1939.

THE SURFACE TENSION OF SLIGHTLY SOLUBLE FATTY ACIDS[1]

By D. G. Douglas[2] and C. A. MacKay[3]

Abstract

Surface tension measurements have been made on normal heptylic, pelargonic, capric, and lauric acids above their melting points and on aqueous solutions of heptylic, pelargonic, capric, and undecylic acids, at various concentrations. A modified capillary rise method was employed. The results indicate that the surface does not reach the stable state at once but requires considerable time, being slower for more dilute solutions and longer chain molecules. Evidence is given for the existence of a monolayer of closely packed molecules, with long axes perpendicular to the surface, each molecule occupying an area of approximately 25 Å for heptylic acid.

Introduction

The properties of the monolayers formed by insoluble long chain fatty acids on water or on dilute acids have been studied in great detail. The short chain soluble acids have also received considerable attention, but the experimental work on the intermediate acids with from 7 to 12 carbon atoms per molecule is still rather meagre (1, Chaps I and II). Two surface properties are of interest:

(*a*) The variation of the surface tension with time.

(*b*) The variation of the surface tension with the concentration of the solution.

For most solutions, the fresh surface reaches an equilibrium or stable condition in a fraction of a second after it is formed, but for some organic solutes the surface may continue to change for much longer periods, up to several hours. This is indicated by the change in the surface tension of soap solutions and solutions of some organic salts and fatty acids in water and in other solvents (2).

The change in the surface tension for varying concentrations of fatty acid solutions has been the subject of a number of papers which are reviewed by N. K. Adam (1, Chaps. I and II) up to the year 1941. Additional references will be given later on in the discussion of the nature of the surface of fatty acid solutions.

Experimental Method and Results

Several methods are available for the measurement of the surface tension for liquid–air interfaces that are slowly changing. We have used one described by Ferguson and Hakes (4), which has several advantages. Although it employs a capillary tube, it is not necessary to have a tube of uniform bore nor need the contact angle be measured. A brief description will suffice. A vertical Pyrex capillary is immersed in the liquid to a known depth. The

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[3] *Professor of Physics.*

meniscus is held at the bottom of the capillary by means of a small air pressure, which is observed on a liquid manometer. Analysis shows that for this arrangement

$$hd = d'(h' - r/3) + 2\sigma/gr, \qquad (1)$$

where h is the manometer reading, d the density of the manometer liquid, d' the density of the liquid under test, h' the depth of immersion of the Pyrex tube, r its inner radius, σ the surface tension, and g the acceleration of gravity. If h is read for several values of h', a graph may be plotted of hd against $(h' - r/3)$, which should be linear. To get the best fit for the experimental points a method given by Goodwin (6, pp. 60–63) was used. It was found necessary to mount the apparatus on a firm base protected from jars or air currents. A large water-bath held the temperature constant. Calibrations were carried out frequently on distilled water, the results being within 0.2 dynes per cm. of the accepted value. The conditions were most favourable late at night, when much of the work was carried on.

To find the change of the surface tension as the surface aged, the depth of immersion of the capillary h' was held constant. A fresh surface was formed by blowing several bubbles of air through it, zero time being taken as the last bubble escaped. Then the air pressure was reduced slightly, to allow the meniscus to ascend a short distance. Since the tension was slowly decreasing, the meniscus gradually descended, and the time at which it reached the tip was recorded simultaneously with the pressure. This procedure was repeated as often as required, so long as no bubble escaped, and from these observations, assuming the density of the very dilute solution to be that of water at the same temperature, the variation of the surface tension with the time was found. Though the surface was not altogether at rest, the results were reproducible unless an accidental jar disturbed the apparatus. The meniscus was descending when the pressure was read, so that the angle of contact between the liquid and the Pyrex tube was very close to zero, a necessary condition for the validity of Equation (1).

Five fatty acids, *n*-heptylic (C_7), *n*-pelargonic (C_9), *n*-capric (C_{10}), *n*-undecylic (C_{11}), and *n*-lauric (C_{12}) were obtained from the Eastman Kodak Company, which were used without further purification. Since few determinations of the surface tension of the liquefied acids are recorded, some measurements were made on four of the five which were available in sufficiently large quantities. The results over a temperature range from 20° to 80° C. are given in Table I and plotted in Fig. 1, where σ is the surface tension in dynes per cm. The melting points of capric and lauric acids were found to be 31.5° and 42.6° C. respectively.

To prepare saturated solutions, an excess of the acid was added to water at 40° C., which was cooled slowly to about 25° C., stirred, and filtered. All fresh saturated solutions showed a surface tension that decreased with the time, but if lauric acid was allowed to stand at room temperature for several hours, the surface tension was just that of water. The other solutions could be stored for several days without losing any of their surface activity. Several

TABLE I

THE SURFACE TENSION OF FOUR FATTY ACIDS

Heptylic C_7		Pelargonic C_9		Capric C_{10}		Lauric C_{12}	
Temp., °C.	Dynes/cm.	Temp., °C.	Dynes/cm.	Temp., °C.	Dynes/cm.	Temp., °C.	Dynes/cm.
22.2	28.60	27.4	28.94	32.0	29.17	44.5	28.71
32.0	27.77	40.0	27.87	43.7	28.15	54.9	28.02
46.0	26.56	51.7	26.98	62.9	26.62	61.4	27.58
59.1	25.48	67.0	25.69	78.0	25.35	78.3	26.48
75.2	24.02						
Temp. coeff. in dynes per cm. per deg. C.							
−0.087		−0.082		−0.083		−0.066	

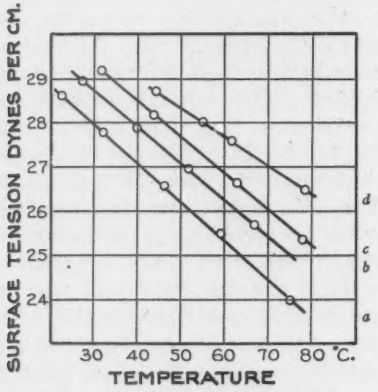

FIG. 1. *The change of surface tension with temperature for four fatty acids: (a) n-heptylic, (b) n-pelargonic, (c) n-capric, (d) n-lauric.*

alkaline solutions of lauric acid were tested. These, when first prepared, showed a surface tension that decreased by about 20 dynes per cm. in 90 min. after the surface was formed, and the same decrease occurred 18 hr. later. This agrees with the work of Powney (7) on a $N/500$ neutral potassium laurate solution, but our results for lauric acid in distilled water do not show the large decrease reported by Fisher and MacKay (5), and none of more than 40 saturated solutions showed any decrease after 8 or 10 hr. Further work is required.

Measurements made on the aqueous solutions of the more soluble, shorter chain acids, C_7, C_9, C_{10}, and C_{11}, under favourable conditions were quite

reproducible. All accidental jars and wind disturbance tended to raise the surface tension to that of water, so that we consider those results which show the lowest surface tension to be most reliable, and only they have been considered. In Fig. 2 the decrease in the surface tension $\sigma_0 - \sigma$ is plotted against the time for four saturated solutions, σ_0 being the surface tension of pure water, σ that of the solution, and the time gives the age of the surface after the last bubble was blown from the capillary. The temperature for all the graphs in the figure was 25° C.

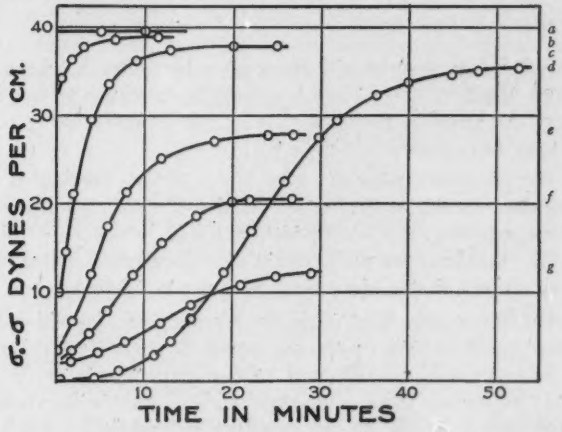

FIG. 2. *The change of surface tension as a surface ages for saturated solutions of four fatty acids: (a) n-heptylic, (b) n-pelargonic, (c) n-capric, (d) n-undecylic. Curves (e), (f), (g) refer to solutions of n-capric acid diluted to one-half, one-quarter, one-eighth of saturation.*

The effect of surface age was also found for three weaker solutions of capric acid, having concentrations of one-half, one-quarter, and one-eighth of saturation, and plotted in Fig. 2. Similar dilutions down to one sixty-fourth of saturation were made for heptylic acid, but for all these the rate at which the equilibrium of the surface was reached was so rapid that we could get only one or two very hurried readings before the surface tension became constant, so that the shape of the graph could not be found. The equilibrium values for heptylic acid are recorded in Table II, in which σ_0 is the surface tension of water at 22° C. and $\sigma_0 - \sigma$ is the decrease at equilibrium due to the acid. The concentration is expressed in terms of that of the saturated solution.

Discussion of Results

The graphs of Fig. 1 show that the surface tension of liquefied fatty acids depends on the length of hydrocarbon chain, lauric having the highest and the others decreasing in the order of the number of carbon atoms per molecule. All have nearly the same temperature coefficient, though heptylic acid gave a slightly more rapid decrease in the surface tension per degree than lauric.

TABLE II

EQUILIBRIUM VALUES OF $\sigma_0 - \sigma$ IN DYNES PER CM.

n-HEPTYLIC ACID SOLUTIONS, VARYING CONCENTRATIONS

Temp. 22° C.

Concentration	Sat.	1/2 sat.	1/4 sat.	1/8 sat.	1/16 sat.	1/32 sat.	1/64 sat.
$\sigma_0 - \sigma$, dynes per cm.	39.8	30.2	21.5	13.3	7.2	2.8	1.1

Our figures are in fair agreement with those given by Adam (1, Chaps. I and II) and Fisher and MacKay (5). They are probably accurate to 0.5 dynes per cm. or better, the possible presence of a slight impurity being one of the factors that may have caused a small error.

Since the shorter chain molecules give lower surface tension, it would be expected that the lowering of the surface tension of saturated solutions would follow the same sequence; this is confirmed in Fig. 2, where $\sigma_0 - \sigma$ is greatest for heptylic (C_7) and least for undecylic (C_{11}). As already stated, the results for lauric acid are not shown since they were not consistent.

It is apparent that surface films of the three fatty acids, for which graphs are drawn, require time to become stable, the longer the chain the greater the time. Even when heptylic acid was diluted to one sixty-fourth of its saturated concentration, its surface gave a constant surface tension in about 10 sec., which was too fast to follow by the capillary rise method. For pelargonic (C_9), capric (C_{10}), and undecylic (C_{11}), the variation of the surface tension could be followed with ease. The increase in $\sigma_0 - \sigma$ is also shown for three dilute solutions of capric acid. The curves suggest that both the concentration and the length of the hydrocarbon chain affect the rate at which the equilibrium of the surface is reached, but that the second factor is more important. More definite results could be obtained if we had been able to measure the concentration, but so far this has not been possible for these exceedingly dilute solutions.

The nature of the film formed by sparingly soluble acids on water has been discussed in a number of papers, most of which are mentioned by Alexander (3). There are two main views, either the film is a monolayer with the COOH head attached to the water surface, or the transition layer from water to acid is several molecules thick. The former is suggested by Langmuir, Adam, and Alexander, while McBain and his co-workers consider that the evidence is in favour of the thicker layer. For insoluble acids above lauric, the Langmuir–Adam trough results are so definitely in favour of the monolayer that there is not much doubt. The film acts as a two dimensional gas, liquid, or solid, depending on the temperature T and pressure per cm. F exerted by the film against a floating barrier. F–A curves have been drawn which are very similar to those for three dimensional gases or liquids, when the area A is

used in place of a volume (1, Chaps. I and II). For large values of F, the graphs of FA against F are almost identical with the well known curves of Amagat for gases at high pressures. Schofield and Rideal (8, 9) have shown that these curves may be deduced from surface tension data for soluble fatty acids where the trough method fails, and that they merge without a break into those for the insoluble films. This is quite strong evidence that both soluble and insoluble acids form monolayers on the surface. Following their method we have carried out the calculations for FA/RT and F for heptylic acid from the data given in Table II. We assumed that heptylic acid is practically undissociated in distilled water. Some previous measurements showed that this is so for capric and is probably nearly true for the others. Schofield and Rideal calculated FA/RT and the mean F corrected for a temperature T_0 of 292° K. The equations that they deduced for these quantities are

$$FA/RT = \Delta \log_{10} C/\Delta \log_{10} F \tag{2}$$

$$F = \sigma_0 - \sigma \text{ (by definition).} \tag{3}$$

$$F' = (0.4343\Delta F/\Delta \log_{10} F)T_0/T$$

where F' is the mean F corrected for temperature.

Using these equations we obtain the results given in Table III.

TABLE III

SURFACE TENSION ISOTHERMAL FOR *n*-HEPTYLIC ACID

n-Heptylic acid at 295° K $\quad T_0 = 292°$ K $\quad T = 295°$ K

Conc.	$F = \sigma_0 - \sigma$	$\Delta \log_{10} C$	ΔF	$\Delta \log_{10} F$	FA/RT	F' at 292° K.
Sat.	39.8	0.301	9.6	0.12	2.5	34
1/2 sat.	30.2	0.301	8.7	0.15	2.0	25
1/4 sat.	21.5	0.301	8.2	0.21	1.4	17
1/8 sat.	13.3	0.301	6.1	0.36	0.8	7
1/16 sat.	7.2	0.301	4.4	0.41	0.7	5
1/32 sat.	2.8	0.301	1.7	0.41	0.7	2
1/64 sat.	1.1					

The isothermal FA/RT against F' at 292° K. for heptylic acid has been plotted in Fig. 3, where curves for lauric and capric, given by Schofield and Rideal, have been added for comparison. There appears to be a regular transition from the shorter to the longer chain acids. The slope of the graph for heptylic acid, about 0.62, is nearly the same as for capric and lauric; this shows that the area occupied by a single molecule in the surface layer is approximately 25 Å for all three independently of the length of the chain. A closely packed film of the insoluble fatty acids has the same molecular area, suggesting that both sparingly soluble and insoluble films have the same structure, with the long axes of the molecules perpendicular to the surface and the COOH head attached to the water.

It may be concluded from these results that surface tension measurements indicate that the surface of sparingly soluble fatty acids on water require

considerable time to become stable, that the time depends on the concentration and the length of the chain, the latter factor being more important, that the surface tension for stable films for shorter molecules is lower than for longer, which is to be expected from measurements on pure acids above their melting points, and finally that the film consists of a monolayer, each molecule occupying about 25 Å and oriented with its axis perpendicular to the surface.

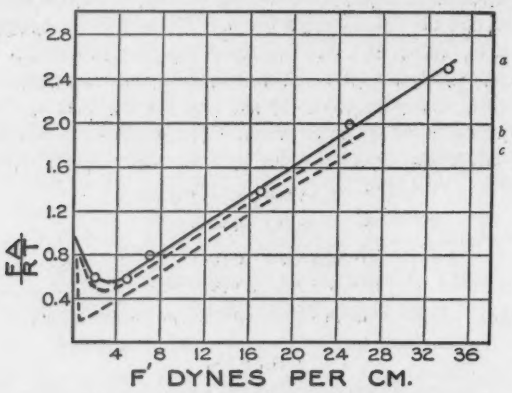

FIG. 3. *Isothermals at 292° K for n-heptylic, n-capric, and n-lauric acids. The full line for n-heptylic acid was obtained by the authors. The dotted curves (b) and (c) are reproduced from a paper by Schofield and Rideal (9).*

References

1. ADAM, N. K. The physics and chemistry of surfaces. 3rd ed. Oxford University Press. New York. 1941.
2. ADAM, N. K. and SHUTE, H. L. Trans. Faraday Soc. 34 : 758-765. 1938.
3. ALEXANDER, A. E. Trans. Faraday Soc. 38 : 54-63. 1942.
4. FERGUSON, A. and HAKES, J. A. Proc. Phys. Soc. London, 41 : 214-223. 1929.
5. FISHER, W. C. and MACKAY, C. A. Can. J. Research, A, 16 : 207-214. 1938.
6. GOODWIN, H. M. Precision of measurements and graphical methods. 1920.
7. POWNEY, J. Trans. Faraday Soc. 31 : 1510-1521. 1935.
8. SCHOFIELD, R. K. and RIDEAL, E. K. Proc. Roy. Soc. London, A, 109 : 57-77. 1925.
9. SCHOFIELD, R. K. and RIDEAL, E. K. Proc. Roy. Soc. London, A, 110 : 167-177. 1926.

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